High pressure and temperature metal-silicate equilibrium in the early Earth: New constraints from moderately (Ga, Sn, and Cu) and highly (Re, Au, Pd, and Pt) siderophile elements

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Recent experimental work and calculations have shown that the primitive mantle abundances of six moderately siderophile elements (Fe, Ni, Co, Mo, W and P) and one highly siderophile element (Re) are consistent with metal-silicate equilibrium at the base of a 700–900 km deep magma ocean in the early Earth (i.e. [1]). Whereas heterogeneous accretion models can successfully explain the chondritic relative abundances of the highly siderophile elements (PGE's, Au), they cannot explain the depletion patterns of the volatile moderately side-rophile elements such as Ga, Sn and Cu (e.g. [2]). This equilibrium magma ocean model must be tested for these highly and moderately siderophile elements. We have initiated systematic studies of three volatile, moderately siderophile elements whose mantle abundances are well characterized, and assess the effect of P, T, f_{O_2} and metal and silicate liquid composition on the magnitude of four highly siderophile elements, Au, Re, Pd and Pt.

Experimental

Experiments have been carried out between 10 and 70 kbar, 1250 to 1750°C in piston cylinder and multi-anvil apparatuses. Basalt powder, doped with Ga_2O_3, SnO_2, and CuO, was used in both types of experiments. Basalt in the piston cylinder experiments was enclosed by FeNiCo capsules, and basalt-FeNiCo mixtures in the multi anvil experiments were encapsulated with graphite. The FeNiCo alloy buffer oxygen fugacities near IW, while graphite buffers about 3 log f_{O_2} units higher. Quenched metals and silicate liquids (glasses) in the run products were analysed for major elements and Ni, Co, Ga, Sn, and Cu by electron microprobe.

Calculation of D(met/sil) as f(P, T, f_{O_2}, X).

It can be shown that increasing pressure causes D(Ga) to increase when all other variables are held constant; D(Cu) shows no change and D(Sn) decreases with pressure. Because pressure is an important variable to quantify, it is clear that it must be accounted for in any attempt to calculate metal-silicate partition coefficients for these three elements. Metal-silicate partition coefficients can be successfully predicted as a function of pressure, temperature, oxygen fugacity, and silicate and metallic melt composition with the expression (from [1]):

$$\ln D \text{ (metal/silicate)} = a\ln f_{O_2} + b/T + c(P/T) + d\ln(1 - X_S) + e(\text{nbo/t}) + f \quad (1)$$

Constants a through f can be calculated by regression of all experimental data, including our new results and previous high temperature and pressure experimental work (see references cited in [3]). For Ga and Sn, the metal-silicate D's are known to be sensitive to Fe/Ni ratio in the metal [4], and thus require attention to activity coefficients (γ) in the metal phase. We have calculated activity coefficients for Ga and Sn using the approach of [4], and regressed against $\ln(\gamma D)$ instead of $\ln D$.

This type of approach (Equation 1) can also be applied to published data for Au, Re, Pd and Pt

TABLE 1. Calculated partition coefficients and mantle abundances (Ga, Sn, Cu in ppm – HSE in ppb)

	D(M/S) low P	D (M/S) high P,T	Measured mantle	Calculated mantle
Ga	3	0.06	1	1.5
Sn	10	0.43	0.1	0.3
Cu	12	0.56	10	20
Re	10^5	820	0.28	0.15
Au*	10^7	620	1.0	0.7
Pd*	10^7	450	3.9	3.8
Pt*	10^9	2300	4.3	1.4
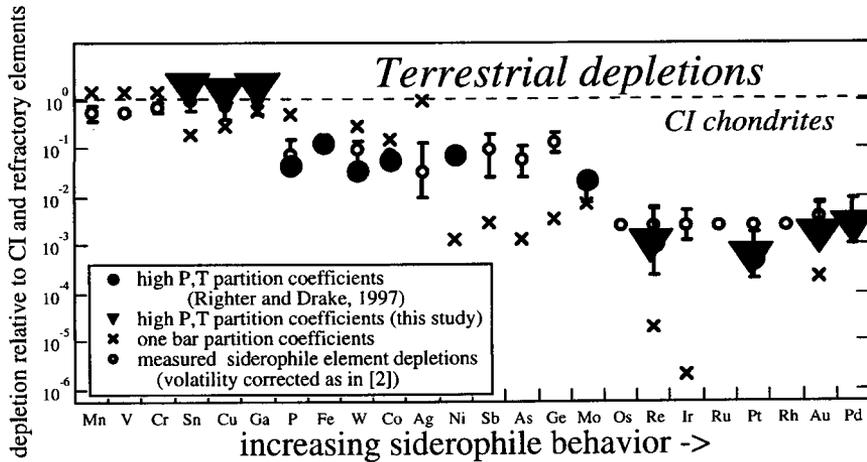
FIG. 1.

(references in [1, 5, 6]). Using such parameterizations, effects of each variable can be isolated; for example, increasing temperature, oxygen fugacity, metallic sulphur content and silicate melt depolymerization clearly cause decreases in metal-silicate partition coefficients for both Pd and Re. Note, however, that the experimental database for the noble metals is small compared to that for the moderately siderophile elements.

Application to Earth

Using these expressions, we can test the hypothesis that the abundances of the moderately siderophile elements, Ga, Sn and Cu, were also set by metal-silicate equilibrium at the base of a deep magma ocean. Calculation of metal-silicate D's for these three elements for the conditions of 1925°C, 250 kb, $\Delta IW = -0.5$, a peridotite magma, and a sulphur-bearing metallic liquid results in D(Sn) = 0.001, D(Ga) = 0.32, and D(Cu) = 0.16. These low values are consistent with the idea that the modest depletion of these elements is due to their

volatility rather than extraction into a metallic core. Similarly, partition coefficients for Au, Re, Pd and Pt can be calculated at the conditions suggested by [1] for metal-silicate equilibrium in the early Earth: P = 250 kb, T = 1925°C, relative oxygen

fugacity – $\Delta IW = -0.5$, metallic sulphur content – $X_S = 0.18$, and silicate melt composition – peridotite (nbo/t = 3.1). Calculated partition coefficients for all four elements approach the values required for equilibrium conditions (Table 1; Fig. 1). Mid-mantle metal-silicate equilibrium provides a better explanation of the mantle abundances of the volatile moderately siderophile elements, and predicts depletions of the HSE elements which are close to measured mantle depletions (Table 1). Further work is necessary on these and other HSE's in order to better constrain the effects of some intensive parameters, especially pressure. This research is supported by NASA grant NAG5-4084.

References

[1] Righter, K. and Drake, M.J. (1997) *EPSL* **146**, 541–53.
[2] Newsom (1990) In: *The Origin of the Earth*, H. Newsom and J.H. Jones, eds., pp. 273–288, Oxford Press, London.
[3] Righter, K. and Drake (1998) *LPS* **XIX**, 1544–45.
[4] Capobianco, C.J., DeAro, J.A., Drake, M.J. and Hillgren, V.J. (1995) *LPS*, **XXVI**, 215–6.
[5] Borisov and Palme (1996) *Mineral. Petrol.*, **56**, 297–312.
[6] Borisov and Palme (1997) *GCA*, **61**, 4349–57.